Recent Progress in Predicting Free Energy of Aqueous Solutes at High Temperatures

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The *ab initio*/classical free energy perturbation (ABC/FEP) method has been used to calculate free energies of aqueous solutes at high temperatures. This method combines the free energy calculated from a classical simulation of an approximate model with the free energy of perturbing the approximate solute-solvent energies into high-level *ab initio* energies. A recent test of this method at 573 K and a water density of 0.725 g/cm^3 gave a hydration free energy for NaCl at infinite dilution of -657 kJ/mol, which is within 4 kJ/mol of the well-known experimental value. The estimated uncertainty in the results (~7 kJ/mol) is mainly due to systematic errors in the quantum method. Pairwise additivity is not assumed and the dielectric constant is not used in the calculation. The method is especially useful in extreme conditions of pressure and temperature, where experimental results cannot be obtained.

This method can also be used to predict association constants of aqueous sodium chloride at high temperatures with an accuracy of about 0.3 log units. A related method can predict the pair correlation function and the co-ordination number of the solute.

These new methods have been used to calculate free energies, pair correlation functions, and running coordination numbers for aqueous Na , Cl-, and the NaCl pair at temperatures from 573 to 973 K and water densities from 0.01 to 0.735 g/cm^3. The resulting free energies and structures of these species in supercritical water will be compared with previous predictions. We find that Lennard-Jones plus charge models of the ion-water interactions are not accurate.